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Control of Mercury Pollution in Sediments

Robert S. Kerr Water Research Center

prepared for

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Control of Mercury Pollution in Sediments

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CONTROL OF MERCURY POLLUTION IN SEDIMENTS

Contract No. 68-01-0087
Project 16080 HTY

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ABSTRACT

Methods are needed for controlling pollution from mercury-laden sediment deposits on the bottom of streams and lakes. The results of exploratory studies to develop such methods are reported here.

Five sediment samples containing from 6 ppm to 500 ppm mercury were investigated. Two samples were taken from the St. Clair River below the outfall of a chloroalkali plant; one sample from the Detroit River below a chloroalkali plant; one sample from a stream which empties into the San Francisco Bay; and one sample from an industrial holding pond used for disposing of waste from a chloroalkali plant.

The geochemical nature of these sediments varied considerably from sample to sample. The major differences were in organic content, sand or silicate content, carbonate content and particle size distribution. Although no effort was specifically directed to determining the chemical form of mercury in the sediment samples, the results of these studies indicate that mercury is present in a variety of chemical forms. These forms likely include mercuric sulfide; complexes with organic materials (proteinaceous or folic acids); and insoluble double salts such as mercury aluminates or mercury ferrates, and adsorbed on particulate matter. The relative amounts of various chemical forms of mercury in a specific sediment depend on what is available in the sediments. Sulfides and organic materials form extremely stable compounds with mercury, and will be the predominant forms of mercury present in the water or sediment. Materials capable of forming double salts are excellent mercury scavengers; however, the compounds are labile and will readily give up mercury in the presence of sulfides or organic complexing agents.

The use of an iron overlay in the form of crushed automobile bodies topped with sand should, on the basis of results developed on this program, be an inexpensive and effective method of isolating mercury-containing sediments from a water overlayer. An important attraction of using iron as an overlay is its ability to reduce methylmercury ions as well as mercuric ions to elemental mercury.

A variety of methods for recovering the mercury values from dredged sediments were explored. Density fractionation, particle size fractionation, flotation, roasting and leaching were the methods studied. Roasting and chemical leaching afford the greatest promise for inexpensive removal and recovery of the mercury. A possible method for in-place leach of sediment deposits is presented.

Field tests of the iron overlay and the chemical leach method are recommended.

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SECTION I

CONCLUSIONS

Mercury lost to streams, rivers and lakes accumulates in bottom sediments. Fish and plants which occupy waters covering these sediments often have a mercury content which approaches the maximum acceptable level for safe consumption by man.

This report describes a method for insulating mercury-laden sediment from its water overlayer, methods for recovering the mercury values from dredged sediment so that it could be used as a safe landfill or returned to the water body, and a possible method for recovering mercury from in-place sediment deposits.

Laboratory studies have shown that scrap iron will rapidly and efficiently remove divalent mercuric ions and methylmercury ions from water by converting these soluble forms to elemental mercury. Hydrated iron oxide which forms when mercury is reduced is an effective precipitating agent for mercury ions. Iron, perhaps as crushed automobile bodies, covered with 4 to 6 in. of sand or other finely divided inert material to prevent erosion and shifting of the iron should serve as an inexpensive yet very effective covering for mercury-laden sediment.

A large fraction of the cost of solving the problem by dredging the mercury-laden sediments would be incurred in transport of the sediment to a site where runoff or leaching of the sediment would not recontaminate a water body, or in the cost of construction of a suitable disposal site. Even if such sites were found or constructed, there would always be a potential hazard posed by these relocated deposits. An inexpensive treatment of the dredgings to recover the mercury value and to sanitize the sediment so that it could be used as a safe landfill or even returned to the water body is desirable.

Roasting, the most commonly used process for recovering mercury from ore, could be used to remove mercury from sediments. Sediments could be roasted without grinding or crushing. Air drying of the sediment prior to roasting would result in a considerable energy saving. Rotary cement kilns are widely distributed and would often be favorably located for sediment treatment. It would be necessary to equip such a kiln with suitable mercury condensation equipment.

Leaching with 1% hypochlorite solution at a pH of 6.0 to 6.5 was found to be very effective for solubilizing the mercury in all but one of the sediments studied. The one exception was the sediment from the San Francisco Bay area, which had a very high organic content. Recovery of mercury from dredgings using this leaching medium appears practical.

Sinkable barges could be used as temporary water-tight cofferdams. A large fraction of the water could be pumped out of the impoundment. The sediment within this impoundment would then be treated with the hypochlorite leach liquid to solubilize the mercury. Mercury would be recovered by reducing with an active metal, by sulfide precipitation or by carbon adsorption.

If in-place treatment proves to be impractical, the portable cofferdam could be used to prevent sediment from being broadly dispersed during dredging. The dredgings could be leached, returned to the water and allowed to settle before moving to the next dredging site.

SECTION II

RECOMMENDATIONS

Two methods are recommended for controlling pollution for mercury-laden bottom deposits. The first method uses a solution of hypochlorite ions (pH 6.0 to 6.5) to leach mercury from dredged sediment or from in-place sediment. The second method uses an iron overlay (crushed or shredded automobile bodies) covered with sand to prevent diffusion of mercuric and methylmercury ions from the sediment into the water overlayer.

Following are specific recommendations for demonstrating each of the methods at a field site.

Method 1 - Hypochlorite Leach of In-Place Sediment

It is recommended that a field demonstration be conducted to:

(1) Demonstrate that hypochlorite solution will solubilize a large fraction of the mercury compounds in natural sediment,

(2) Determine the optimum concentration and pH of the hypochlorite solution for leaching in-place sediments,

(3) Determine the rate of leaching and the amount of sediment agitation required to achieve efficient leaching, and

(4) Develop and evaluate methods for recovering the mercury from the leachate.

A site should be selected where the water level, the water inflow and the water outflow can be controlled. An industrial holding pond would be an appropriate site. Recovery from dredged sediment could be substituted for in-place recovery.

A detailed outline for a field test of this method is attached to this report as an Appendix. Preliminary estimates of the cost of recovering mercury by this method vary from $5,000 to $10,000 per acre depending on the site.

Method 2 - Iron Overlay

It is recommended that a field demonstration be conducted to: (1) demonstrate that an iron overlay covered with sand is an effective barrier and will prevent mercury from diffusing out of the sediment into the water, and (2) determine the long-range environmental effects of an iron-sand overlay on the flora and fauna of the water body.

A site to field test this method must be carefully selected. The water inflow should be essentially mercury-free. The flora and fauna of the water body must not contact sediment not covered with the overlay. A control site must be operated under identical conditions to demonstrate the effectiveness of the treatment.

It is recommended that ponds be constructed specifically for this study. These pond bottoms will be covered with 4 to 6 in. of mercury-spiked natural sediment for demonstration purposes. The sediment in one pond would be covered with 4 to 6 in. of iron and then with 4 to 6 in. sand; in a second pond the sediment would be covered only with sand. A control pond would contain only spiked sediment.

The ponds would be filled with fresh water, appropriate flora and fauna introduced into the ponds and monitored for mercury accumulation over an extended time interval. These same ponds could be used to study the uptake of other heavy metals or pesticides by the flora and fauna of a water body.

A detailed program outline for a field test is contained in the Appendix. Preliminary estimates of the cost of treating mercury-laden sediment by this method is $2,500 to $3,000 per acre.

SECTION III

INTRODUCTION

Midwest Research Institute has been conducting studies to develop methods for controlling pollution from mercury-laden sediment by isolating or decontaminating sediments present in the bottom of lakes and rivers. These sediments are potentially serious health hazards since they are believed to be the source of mercury found in fish inhabiting the waters overlaying these sediments. It is further believed that the highly toxic methylmercury found in fish tissue is formed by organisms present in the sediments. This program, funded under EPA Contract No. 68-01-0087, was initiated to evaluate methods for isolating mercury-laden sediments from the water overlayer, for decontaminating sediments in place, and for recovery of mercury from sediments removed from the bottoms of water bodies.

Two attractive approaches for treating these sediments have been investigated: (1) An iron overlay (perhaps using crushed automobile bodies) covered with sand, clay, or other environmentally acceptable material to prevent mercury from entering the water overlayer was evaluated. The results of these studies showed that iron will remove soluble mercury from water by converting it to elemental mercury. Iron also reduces toxic methylmercury ion to elemental mercury, and should function as an effective barrier preventing any methylmercury formed in the sediment from entering the water overlayer and contaminating the flora and fauna of the water body. (2) A method using a hypochlorite leaching solution (pH 6.0 to 6.5) for removing mercury from dredged sediments was investigated. This treatment would allow the treated dredgings to be returned to the water body or used as landfill without fear of contamination. Design and construction of portable cofferdams would allow the sediments to be treated in place to remove and recover the mercury.

Following is background information relevant to experimental studies of methods for coping with the mercury pollution problem.

Approximately 83,000 tons of mercury have been consumed in the United States during this century.[1] However, little information is available on how and where it entered the environment. The largest source of industrial mercury pollution in 1968 was chloroalkali plants.[2] By 1970, the levels of mercury emissions from these plants had decreased by 86%. Similar improvements have been made by other industries in reducing mercury effluents. Of the total of 2,865 tons of mercury purchased in the U.S., in 1968, 76% or 2,160 tons were lost to the environment. This loss does not include that amount emitted to the atmosphere during mercury ore refining (approximately 31 tons/year), or mercury emitted as a by-product of tin, zinc, copper and gold production. Mercury emissions from coal combustion, probably the

largest source of mercury emission into the air, is estimated at anywhere from 275-1,800 tons/year. From these major sources, some 2,500-4,000 tons of mercury were lost to the environment in 1968. The reduction in losses from various industries since 1968 would reduce this figure; however, consumption of coal by electrical industries has increased. The majority of this mercury eventually ends up in the sediment of lakes, rivers and oceans.

Other sources of mercury in the environment can be traced to mercury ore deposits and brackish water runoff from oil fields. These sources often result in high natural background levels of mercury in the affected areas.

Alkylmercury salts, in general, and methylmercury, in particular, are the most hazardous forms of mercury in the environment; the inorganic forms of mercury are much less hazardous. All serious incidents of mercury-poisoning can be traced to losses of man-made alkylmercury compounds to the environment.

It is generally accepted, although poorly documented, that methylmercury is biologically formed in the sediments which contain mercury. It is postulated that methylmercury thus formed is absorbed by microscopic plants and animals, and then works its way up the food chain. It is also probable that methylmercury present in water would be absorbed directly through the gills of fish.

Homogenized fish tissue has been used as a source of organisms that will methylate mercury. It has also been demonstrated that chickens can methylate mercury *in vivo*.[3] It therefore seems probable that fish are capable of methylating mercury *in vivo*. The mercury can be made available for methylation by ingestion, adsorption in the gills, or absorption on the outer surface of the fish. Absorption of inorganic mercury on the intestine walls or on other fish surfaces is thermodynamically probable since proteinaceous material forms very stable coordination compounds with divalent inorganic mercury. Hence, an important consideration which will determine the usefulness of a mercury decontamination method is whether methylmercury found in fish is primarily obtained from the food they eat or by *in vivo* methylation.

Although much more information is needed to describe the metabolic processes responsible for methylmercury accumulation in fish tissue, two facts are incontrovertible: (1) mercury is present in substantial quantities in the sediment in some water bodies; and (2) fish in these same water bodies contain abnormally large quantities of mercury.

The chemical composition and physical properties of sediments are known only in a very general manner. They contain varying quantities of igneous rock, sedimentary rock and other geophysical products. Individual particles range from submicron to multicentimeter in dimension. Sediment contains, in

addition, particles of waste solids, and liquids that have been added by industrial operations and other human factors. In short, each sediment bed is a peculiar mixture of materials. In a technical sense, each sediment bed is a raw material which may require a unique series of processes and operations to remove mercury.

The chemical forms of mercury contained in sediment have been deduced from isolated chemical examinations of relatively simple systems in the laboratory. The factors that affect the state of mercury in contaminated sediments, however, are poorly understood at this time, primarily because little attention has been directed to defining the chemistry of these types of materials.

Based on this information, the hazard of mercury contaminated sediment could be reduced by: (1) Isolation of the mercury-laden sediment from the water overlayer. This method of dealing with the mercury problem is probably a holding action at best and is most applicable to situations where mechanical disturbance or erosion of the sediment is expected to be minimal. (2) Removal of mercury compounds from the bulk of materials in the sediment removed (dredged) from the water body or recovering the mercury compounds from the sediment in place, perhaps by treating one section of the system at a time.

The second method could utilize modified forms of metallurgical processes now used in recovering metal values from ores, or in some instances, seawater and brines. It follows that the technology of mercury hydrometallurgy can be adapted, with appropriate modifications dictated by the nature of the raw material, to the problems encountered in handling and processing mercury-laden deposits.

New and more subtle methods for dealing with mercury-laden sediments may present themselves as additional information on physical, chemical and biological processes operative in the sediments, the water, and in aquatic life is developed.

SECTION IV

EXPERIMENTAL DESIGN AND RATIONALE

The experiments conducted and the rationale behind these experiments were based on our understanding of the mercury contamination problem. Experimental studies were sometimes modified during this program as new insight into the nature of the problem was developed.

Following are descriptions of the sediments studied, a discussion of the experimental rationale, and details of methods of analysis.

Descriptions of Sediment Samples Studied

The results of work in this program are based on information about the states of mercury in sediment for five sources: two from the St. Clair River; and one each from the Detroit River, the Islais Creek which flows into the San Francisco Bay, and an industrial waste impoundment.

One sample from the St. Clair River and the sample from the Detroit River were supplied by the EPA Grosse Ile Laboratory. A sample from Islais Creek was supplied by the Corps of Engineers, and the remaining two samples were furnished by private industries. Table 1 contains information on the samples.

The major portion of the effort was devoted to Samples 1 and 5 because of their high mercury content. Sample 2, which was obtained late in the program, received very limited attention.

Samples 1 and 3 were collected and shipped as individual grab-samples. Since more than one grab-sample was required to complete a series of mercury recovery studies, all the grab-samples were combined into one large sample. The initial studies conducted on St. Clair Sample 1 were an exception. A single grab-sample containing approximately 37 ppm mercury was used. That sample is designated Sample 1a throughout this report. The combined grab-samples (Sample 1) had an average mercury content of 127 ppm.

All samples were thoroughly mixed before studies were initiated.

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TABLE 1. SEDIMENT SAMPLES

Sample Source	Sample Number	Sampling Method	Sample Size	Remarks
St. Clair River 33.5-mile point	1	Peterson Dredge	9 - grabs (~ 3 gal.)	Near Canadian shore 40% ooze, 40% silt, 20% clay Considerable variation (37 - 130 ppm) in mercury content between grab samples.
St. Clair River	2	Unknown	5 gal.	Near Canadian shore Mercury content ~ 25 ppm.
Detroit River	3	Peterson Dredge	5 - grabs (~ 1.5 gal.)	Sample taken 20 ft from U.S. shore at 13.1-mile mark. Mercury content 6.5 ppm.
Islais Creek, San Francisco Bay	4	Unknown	5 gal.	Mercury content 6.9 ppm.
Industrial Pond	5	Unknown	5 gal.	Mercury content > 500 ppm.

Experimental Rationale

Iron Overlay. The rationale behind using iron as an overlay for mercury-contaminated sediment to prevent mercury entry into the water overlayer was based on both chemical and biological considerations. In the chemical sense, iron is sufficiently active to reduce mercurous, mercuric and methylmercury ions. The electrochemical potentials for these reactions are expressed as the Gibbs free energy (ΔG) for the reactions. (No free energies of formation for the methylmercury ion could be found.)

$$3\ Hg^{+2} + 2\ Fe^{0} \longrightarrow 2\ Fe^{+3} + 3\ Hg^{0} \qquad \Delta G = -123.2\ \text{Kcal/mole}$$

$$3\ (Hg)_2^{+2} + 2\ Fe^{0} \longrightarrow 2\ Fe^{+3} + 6\ Hg^{0} \qquad \Delta G = -113.8\ \text{Kcal/mole}$$

Although the free energies values indicate the driving force for the reactions, the rates of reaction are equally important and must be determined experimentally. Hence, preliminary in-house studies were conducted to demonstrate that the rate of reaction was sufficient to warrant using iron as an overlay. Preliminary studies also demonstrated that iron would remove methylmercury ions from water.

The reduction of methylmercury greatly increased the attractiveness of the iron overlay since it is widely believed that methylmercury is formed in the sediment and then works itself into the biota of the water body.

The product of reduction by iron is hydrated ferric oxide. This oxide is a good coprecipitator of mercuric ions. Hydrated ferric oxide is relatively insoluble, is widely distributed in water, and is not considered to be an environmental hazard. Municipal water treatment methods commonly remove most iron salts from water. Discarded automobile bodies are plentiful and inexpensive, and are suggested as the overlay iron source. Within funding and time limitations imposed on this program, it was determined that program objectives could best be met by determining the efficiency and the rate of iron reduction of mercuric and methylmercury ions and by identifying factors which affect the reduction such as pH, light, oxygen and the presence of interfering compounds. Studies were therefore designed to generate this information.

Mercury Recovery from Sediment. Removal of mercury from contaminated sediment has been suggested in a number of cases as the most desirable solution to the problem. Dredging has been suggested as a plausible solution to a few specific problems; however, an in-place treatment would offer many obvious advantages if a practical method could be devised.

This report does not address itself to the environmental consequences of dredging, and definitive studies addressed to this issue are recommended before widespread dredging is initiated to alleviate the mercury problem. Total mercury removal may be the only answer in situations where bottom agitation would make an overlay impractical. A variety of physical and chemical methods for separating mercury from the sediment were investigated.

Following are descriptions of physical and chemical separation methods investigated.

Particle Size Separation. Size grading is a commercially practiced method used widely by mineral processing and food industries. Size grading to -325 mesh is routine. There has been considerable speculation that mercury in sediment is primarily associated with the fine particles. If a large fraction of the mercury were in these fines, then sieving might be used to concentrate the mercury in a small fraction of the sediment. Hence, Samples Nos. 1, 3, and 4 were separated into four particle-size fractions by sieving. Each fraction was weighed and its mercury content determined.

Gravity Separation. There are many examples of purification processes based on transport and settling of particles of different densities. Placer mining for gold recovery is a prime example. In modified forms the technique has been adapted to numerous industrial processes, particularly those in which water can be utilized.

There has been isolated evidence[4/] that mercury is concentrated in a high-density fraction of the sediment. Hence, density fraction offered a possibility for separating the mercury-containing fraction. If the mercury were predominantly in the high density fraction, then perhaps agitation of the sediment and subsequent settling would result in stratification, with the mercury in the bottom strata covered by relatively clean sediment. Such a condition might effectively insulate the mercury from the water overlayer.

Sediment Samples Nos. 1, 3, 4, and 5 were divided into a number of specific gravity fractions by placing wet sediment samples in centrifuge tubes containing mixtures of carbon tetrachloride and tetrabromoethane. By varying the proportions of the two liquids, a range of specific gravities from 1.6 (pure CCl_4) to 3.0 (pure $C_2H_2Br_4$) was obtained. Wet sediment was agitated violently with the solutions and the mixtures then centrifuged for several minutes at 2,000 rpm. The material more dense than the liquid settled to the bottom, and the less dense material floated. Beginning at the low density end, successive specific gravity fractions were collected and analyzed for total mercury.

Flotation. Air flotation is a standard method used in mercury mining for upgrading the mercury sulfide ore from 0.2-0.5% to 55-60%. It has been postulated that mercuric sulfide is the principal form of mercury present in the sediment of rivers and lakes. As a consequence, flotation was investigated for removing mercury from sediment. Two reagents (Roccal and Zephiran) are commonly used in flotation of mercuric sulfide.

Approximately 1 lb of sediment was placed in a Denver Sub-A 500-g flotation cell. The cell was Teflon coated prior to initiating these studies to minimize reduction of any water soluble mercury ions on the walls of the flotation cell.

A variety of activators, promoters, and frothers were investigated. These include Zephiran, Roccal, pine oil, aerosol OT and Saratoga chips. The floats were collected, weighed and analyzed for mercury.

Pyrometallurgy. The most commonly used process for recovering mercury from ore is roasting. The process consists of heating cinnabar to reduce and volatilize the metal followed by condensation of the vapor. Either mechanical furnaces or retorts are used to roast the mercury-bearing materials. The process is continuous in a mechanical furnace, and batch in a retort. Roasting is so efficient for recovering mercury that beneficiation prior to roasting is needed only for low grade ores. Ore taken from open cast mines commonly contains 0.1-0.15% mercury. Since some isolated sediments have mercury contents approaching this level, it may be economically feasible to decontaminate such sediments by roasting.

A limited number of roasting studies were conducted to determine whether mercury would be efficiently reduced and volatized from sediments without beneficiation. Treatment of dredged sediment by this method might be feasible where surplus kilns (such as a large rotary kiln from a cement plant) could be equipped with a suitable mercury condenser and used locally to treat sediments.

Sediments were roasted both in the presence and absence of air, and then analyzed for total mercury.

Chemical Leaching. Hydrometallurgical processing has not been used extensively to extract mercury from cinnabar. However, one accepted process uses a solution of sodium sulfide and sodium hydroxide which solubilizes metallic mercury or cinnabar. The mercury is generally believed to be present in sediment as a sulfide. However, a significant fraction is present as a complex with organic materials (amino acids or folic acid) or adsorbed on particulate material, either organic or inorganic. Mekhonina[5] reported the distribution of Mercury II between phases in organic matter-water

and mineral matter-water systems as a function of pH. His studies indicated that a large fraction of mercury in sediment might exist as a complex with both organic and mineral matter. These complexes would reportedly dissociate at a low pH (6.3) to yield water soluble mercury.

Studies were conducted to determine whether mercury in the sediment samples studied on this program could be solubilized. The effectiveness of hydrochloric, sulfuric, and nitric acids were investigated as a function of pH and temperature. Hydrochloric acid affords the added advantage of chloride ions which allow formation of the water soluble $HgCl_4^{-2}$ complex. Nitric acid was studied because of its oxidizing potential, and sulfuric acid because it is most economical. The effect of adding chloride, as sodium chloride, to sulfuric acid was determined. A hydrometallurgical process using hypochlorous acid (pH 6-6.5) for extracting mercury from low grade ore was investigated. The effectiveness was determined as a function of pH, hypochlorite concentration and leach time.

The sediments were dispersed in the appropriate solutions and the solutions agitated. Samples of the leachate were taken at various intervals and centrifuged to remove suspended solids. The clear supernatant was digested in aqua regia and analyzed for total mercury. At the end of each leaching study the sediment was digested and analyzed for total remaining mercury.

Analytical Procedures

The step-by-step procedures used in analyzing for total mercury, methylmercury and dimethylmercury are:

Total Mercury.

(1) Twenty milliliters of aqua regia slowly added to ≤ 5 g of wet sediment in a 100-ml beaker.

(2) Allow the mixture to stand at ambient temperature until no evidence of reaction can be detected.

(3) Boil sample for 2 min.

(4) Cool sample and transfer to polyethylene centrifuge tube.

(5) Mix with vortex.

(6) Centrifuge and then decant liquid into 100-ml volumetric flask.

(7) Wash sediment with 20 ml of water, centrifuge and combine liquid with (6).

(8) Repeat (7).

(9) Dilute sample to 100 ml.

(10) Add 2 ml $SnCl_2$ (10% solution) to a suitable aliquot of (9).

(11) Aspirate sample through 10-cm AA cell.

The instrument used for these analyses was a Varian AA-5 Atomic Absorption Spectrometer.

Water samples to be analyzed for mercury were treated by the same procedure as sediment. The purpose of the treatment was to free the mercury from suspended solids that may have been in the liquid. Steps (7) and (8) were omitted in water analyses.

Methylmercury. Methylmercury analyses are more difficult. The amount of methylmercury which can be recovered from a sample is very dependent on the chemical nature of the sample. Fish tissue and some sediments seem to hold methylmercury tenaciously. The procedure for extracting methylmercury and the workup for analysis used in this laboratory is as follows:

(1) Add acidified KBr (5 ml) solution to sample to free methylmercury. (This solution contains 100 g concentrated H_2SO_4, 310 g KBr in 1 liter of solution.)

(2) Extract with 35 ml of toluene and centrifuge.

(3) Freeze aqueous layer and pour off toluene.

(4) Extract toluene with aqueous cysteine. (This solution contains 10 g cysteine, 7 g sodium acetate and 125 g sodium sulfate in 1 liter of solution.)

(5) Repeat step (4).

(6) Add 0.6 ml of 3 molar KI to extract.

(7) Extract water solution with 2 ml of benzene.

(8) Store in dark freezer if analysis is delayed.

(9) Analyze by gas chromatography.

The GC conditions for methylmercury analysis were:

(1) Column 3 to 4 ft, 0.25-in. glass column.

(2) Packing - OV 17 (1.5%)/QF-1 (1.95%) on Supelcoport 100/120 mesh.

(3) Carrier - Nitrogen, approximately 70 ml/min.

(4) Temperature - Inlet - 180°C
- Column - 115°-130°C depending on column length
- Detector - 165°C

(5) Detector - Electron capture (tritium foil), polarizing voltage 12 V.

Dimethylmercury. Dimethylmercury is analyzed as methylmercury. Samples suspected of containing dimethylmercury must be stored in the dark because of its sensitivity to light. Dimethylmercury is not likely to be found in samples containing mercuric ions since the two rapidly disproportionate to form methylmercury.

(1) Extract sample with toluene.

(2) Reflux while stirring equal volumes of toluene and aqueous $HgBr_2$-KBr solution. (This solution consists of 15 g $HgBr_2$ and 100 g KBr in 1 liter of solution.)

SECTION V

EXPERIMENTAL RESULTS

The experimental program was divided into two phases: (1) overlay of mercury-laden sediment with iron; and (2) recovery of mercury from sediment. Studies were designed to identify the important variables and to optimize the conditions for each of these methods of treating hazardous mercury-laden sediments.

Overlay of Mercury-Laden Sediments with Iron

The use of an iron overlay to prevent water soluble inorganic or methylmercury ions from entering water over a mercury-contaminated sediment was based on studies that had been conducted at MRI prior to this program which showed that both types of ions were effectively reduced by iron turnings. The Gibbs free energy for the reduction of the methylmercury ion was unknown. The rate of the reduction was not known for either inorganic or methylmercury ions.

Iron Reduction of Mercuric Ions. Studies of the reduction of mercuric ions (mercuric nitrate) in an aqueous media were conducted under a variety of conditions which might exist in nature. These conditions included variations in pH; reduction in the presence of interfering substances, such as chloride ions which form the stable complex $HgCl_4^{=}$; and reduction in the presence and absence of oxygen. The results of studies of mercuric ion reduction by iron are shown in Table 2.

Methylmercury reduction by iron turnings was studied at pH values of 7.3, 6.0, 4.0, and 2.6 in the presence and absence of oxygen, and in the presence and absence of light. High initial concentrations of mercuric and methylmercury ions in water (> 100 ppm) were used in early studies. In later studies, starting concentrations of 5-7 ppm were used. In all these studies approximately 10 g of iron turnings (1/6 in. x 1/4 in. x 1 in.) was placed in a round-bottom flask. The iron filings were cleaned first with acetone, washed with distilled water and then with 5% nitric acid, and again with distilled water. The mercury solution was prepared by diluting a 500-ppm mercury solution to the desired volume (1 liter) adjusting the pH by adding sodium hydroxide or nitric acid, then adding any desired foreign ions or compounds.

TABLE 2. MERCURIC ION REDUCTION BY IRON

Experiment	pH	Reaction Time (min)	Total Hg^{++} in Water (ppm)	Percent Hg Removed	Remarks
1(a)	6.3	0	69.0	-	O_2 Atmosphere
	6.3	2	67.0	3.0	
	6.3	5	51.0	26.0	
	6.3	12	34.0	50.7	
	6.2	25	34.0	50.7	
	6.3	45	46.0	33.4	
	6.3	105	46.0	33.4	
2(a)	9.6	0	78.0	-	
	9.6	2	63.0	19.3	
	9.6	5	59.0	24.4	
	9.6	11	52.0	33.4	O_2 Atmosphere
	9.6	25	49.0	37.2	
	9.6	45	47.0	39.9	
	9.2	90	55.0	29.5	
	-	185	58.0	25.7	
3	8.1	0	80.0	-	
	8.1	1	55.0	31.3	O_2 Atmosphere
	8.1	5	58.0	27.5	Agitation stopped after 180 min
	8.0	11	45.0	43.8	
	7.6	26	39.0	51.3	
	7.6	60	40.0	50.0	
	6.7	120	40.0	50.0	
	6.8	180	38.0	52.5	
	-	1,200	0.2	99.8	

TABLE 2 (Concluded)

Experiment	pH	Reaction Time (min)	Total Hg^{++} in Water (ppm)	Percent Hg Removed	Remarks
4	4.0	0	117.0	-	
	-	16	48.0	59.0	O_2 Atmosphere
	5.4	134	6.6	94.4	With 1% Cl^-
	-	1,108	0.56	99.5	
					Agitation stopped after 134 min
5	4.0	0	0.68	-	
	-	150	0.40	41.2	O_2 Atmosphere
6	4.0	0	78.75	-	
	-	55	0.4	99.5	N_2 Atmosphere
	-	125	0.515	99.4	
7(b)	2.5	0	10.0	-	
	-	15	4.2	58.0	
	-	240	0.8	92.0	

(a) Solutions found to contain dispersed elemental mercury.

(b) Solution passed through a 1.25 in.x 9.25 in. column packed with iron turnings.

The solution was placed in a 2-liter, 3-necked round-bottom flask and the iron turnings added. When studies were conducted in an oxygen-free atmosphere, the reactor was purged for 1 hr with nitrogen, while being stirred with motor-driven polyethylene paddles. A number of interesting observations regarding the reduction of mercuric ions by iron were made during these studies. The amount of mercuric ions reduced and removed from the water during Experiments 1 and 2 were considerably below the amount which had been removed in earlier in-house studies. The only significant difference between the experimental procedures was the amount of agitation of the reaction system. In the earlier studies, the mixture was gently agitated on a rocker. In Experiments 1 and 2, the reaction media were vigorously stirred with a polyethylene paddle at 350 rpm. This rather violent agitation was apparently sufficient to cause the elemental mercury condensed on the iron to be redispersed, since 50-70% of the mercury in the water at the end of these experiments was determined to be elemental mercury. Finely divided elemental mercury is very susceptible to air oxidation. Continuous reoxidation of this finely dispersed elemental mercury by air probably accounted for the unexpectedly large amount of ionic mercury present in the water phase at the end of the experiment. When agitation of the reaction medium was stopped and the dispersed particles allowed to settle as shown in Experiment No. 3, the mercury content of the water dropped dramatically.

Hydrated iron oxide is an excellent coprecipitator for heavy metals such as mercury. A significant fraction of the mercury found in the aqueous phase in Experiments 1 and 2 may have been associated with finely divided hydrated iron oxide. Beginning with Experiment No. 3, all samples were centrifuged to remove finely divided suspended material. In all succeeding studies the samples were centrifuged before analysis, and all contained < 1 ppm mercury at the end of the experiment.

Solubility and thermodynamic considerations indicated that 0.2-0.8 ppm mercury was more than should have been present in these samples. It therefore seems likely that a significant fraction of the < 1 ppm mercury found in water at the end of the experiments was present as either solubilized elemental mercury, colloidally suspended elemental mercury, or colloidally suspended hydrated iron oxide containing absorbed mercury.

A large fraction of the remaining mercury (0.2-0.8 ppm level) was removed when the water was passed through micropore filters. However, these filters absorb mercuric ions, and the results of this analysis still do not indicate whether the approximately 0.5 ppm of mercury was present as suspended particulates containing mercury or as solubilized mercuric ions.

Lower initial concentrations of mercury in water did not significantly affect the final mercury content of the water. There is some indication that the efficiency of mercury removal is better at a pH of 8 (Experiment 3) than at lower pH values.

When the results of Experiment 4 (run in an air environment), and Experiment 6 (run under a nitrogen atmosphere) are compared, it appears that oxygen reduces the rate of mercury removal. Thus, it appears that an anaerobic condition in the region of the iron overlay might be beneficial in preventing mercury from diffusing from the sediment, through the iron overlay into the water overlayer.

Iron Reduction of Methylmercury Ions. The same procedure was used for both mercuric ion and methylmercury ion reduction studies. However, in later studies of methylmercury, the purging gas was passed through toluene traps to collect any dimethylmercury formed. The results of studies of methylmercury reduction by iron are shown in Table 3. Table 4 shows the amount of methylmercury converted to dimethylmercury.

The amount of reduction which had occurred was determined by analyzing the water for total mercury. A 20-ml aliquot of water was taken from the reaction vessel. The sample was centrifuged for 2 min at 2,000 rpm to precipitate suspended solids. An aliquot of the supernatant was then carefully collected and digested in boiling aqua regia before being submitted for analysis by atomic adsorption spectroscopy. Investigators at Dow Chemical Company recommended using micropore filters to remove suspended solids from water samples before analysis. Studies conducted in this laboratory indicated that those filters will absorb microgram quantities of mercury from dilute aqueous solutions.

All samples taken for analysis were stored under acid conditions in acid-washed polyethylene bottles to minimize mercury absorption on the walls of the storage vessel.

The results of studies reported in Table 3 indicate that the reduction will occur either under aerobic or anaerobic conditions. The reduction was studied both in the presence and absence of oxygen since either conditions could exist at a water-sediment interface, and because Keevay and Hansen[6] had observed that oxygen increased the rate of degradation of methylmercury by acid by a factor of 10^3. No attempt was made to obtain good rate data on this degradation. It was felt that methylmercury formed in nature would have to diffuse through the iron overlay, and would therefore be in contact with the iron several hours or days. Based on the results of these studies, such contact time appears to be adequate to reduce and degrade the methylmercury.

Dimethylmercury is decomposed by ultraviolet radiation.[7] Experiment 6 was conducted in the dark because of the possibility of light affecting the reduction of methylmercury by iron and because little or no light would be present at the sediment-iron interface where the reduction of methylmercury would occur. The results indicated that the reaction does not require photoexcitation.

TABLE 3. REDUCTION OF CH_3Hg^+ BY IRON

Experiment	pH	Atmosphere	Reaction Time (hr)	Total Hg (ppm)	Hg Removed (%)
1	4.0	Air	0.0	77.0	-
			0.1	40.0	48.1
			0.4	11.0	85.8
			1.0	9.8	87.3
			2.8	16.8	78.9
			29.4	0.56	99.3
2	6.0	Air	0.0	101.5	-
			0.1	35.0	65.6
			0.4	13.0	87.2
			1.4	35.0	65.6
			2.4	0.96	99.1
			25.8	0.11	99.9
3	4.0	N_2	0.0	103.0	-
			2.8	110.0	
			18.4	112.0	
			18.7	107.0	
4	2.6	N_2	0.0	230.0	-
			2.0	50.5	78.1
			16.0	9.3	96.0
	2.6	Air	16.5	3.4	98.6
			20.0	2.2	99.1
			24.5	1.4	99.4
			24.5[a]	6.5	97.2
5	4.0	N_2	0.0	95.5	-
			1.0	10.3	89.3
			3.0	12.5	87.0
			6.0	19.0	80.2
6[b]	4.0	N_2	0.0	34.5	-
			0.5	3.6	89.6
			4.0	3.0	91.4
			20.2	1.5	95.7
7	7.3	N_2	0.0	8.8	-
			0.5	8.2	6.9
			2.0	5.9	33.0
			4.0	2.5	71.6
			19.5	1.9	78.5
8	7.3	Air	0.0	8.6	-
			0.6	5.0	41.9
			2.0	4.6	46.6
			4.1	6.0	30.3
			21.5	4.6	46.6

TABLE 3. (Concluded)

Experiment	pH	Atmosphere	Reaction Time (hr)	Total Hg (ppm)	Hg Removed (%)
9(c)	7.3	Air	0.0	7.9	-
			0.5	7.0	11.4
			2.1	7.3	7.6
			3.7	7.1	10.2
			67.0	6.1	22.8
			91.0	4.9	38.0
			116.0	2.8	-
			124.0	0.9	67.8
			142.0	0.54	80.8
10	-	Air	0.0	7.56	-
			20.0	0.56	92.6
			92.0	0.06	99.3
			116.0		
			140.0	0.076	99.0
			164.0	0.041	99.5
			188.0	0.066	99.2
11	-	N_2	0.0	7.4	-
			32.0	0.39	94.8
			56.0	0.057	99.2
			80.0	0.036	99.5
			152.0	0.034	99.5
			176.0	0.034	99.5
			200.0	0.017	99.8

(a) Sample not centrifuged before analysis.

(b) 12 ppm Cysteine hydrochloride added to system.

(c) Experiment shielded from light.

TABLE 4. CONVERSION OF CH_3Hg^+ TO $(CH_3)_2Hg$ BY IRON

Experiment	pH	Atmosphere	Total CH_3Hg^+ (Mg)	$(CH_3)_2Hg$ Formed (Mg)	Percent Theoretical
7	7.3	N_2	2,700	175	13.0
8	7.3	Air	2,700	75	5.6
9	7.3	Air	2,578	75	6.1
10	-	Air	2,700	385	28.5
11	-	N_2	2,700	300	22.2

Reducing agents and strong complexing agents are known to convert alkylmercury ions to dialkylmercury. Since the atmosphere over these reactions was controlled by passing either air or nitrogen through the reactor, this carrier gas was simply passed through toluene traps to collect any dimethylmercury being formed.

In Experiments 7, 8, 9, 10, and 11, dimethylmercury was found in the trap. The reaction to form dimethylmercury is:

$$6CH_3Hg^+ + 2Fe \longrightarrow 3(CH_3)_2Hg + 3Hg + 2Fe^{+3}$$

However, any mercuric ion present in the system will undergo a disproportionation reaction with dimethylmercury to convert it back to methylmercury. This reaction is rapid and quantitative.

$$(CH_3)_2Hg + Hg^{+2} \longrightarrow 2CH_3Hg^+$$

In all of the experiments, 30% or less of the methylmercury was converted to dimethylmercury (theoretical is 50%).

Although a relatively large fraction of the methylmercury was converted to dimethylmercury in these concentrated reaction systems, formation of dimethylmercury in nature should not be a problem since only very small equilibrium quantities of methylmercury would be present and because the reaction involves a methyl transfer, that is, it requires two methylmercury ions coming together simultaneously to affect the methyl transfer. There would likely be sufficient divalent mercury present to react with any dimethylmercury and convert it to methylmercury.

Laboratory Evaluation of Iron Overlay of Sediments. A series of experiments was conducted to evaluate the effectiveness of the iron overlay. Sediment Samples 1, 3, 4, and 5 were studied as follows:

(1) Approximately 1 lb of each sediment was placed in each of three 1-gal. wide-mouth glass jars.

(2) One sample of each sediment was covered with distilled water.

(3) A second sample of each sediment was covered with approximately 1 in. of iron turnings and then with distilled water. These turnings were several feet long and were compressed into a loose overlay.

(4) The third sample of each sediment was covered with 1 in. of iron turnings, 1 in. of mercury-free sand, and then with distilled water. The

samples were rocked gently through an arc of about 30 degrees at a rate of 10 rocks/min. These conditions were used to simulate wave motion over a sediment in the bottom of a lake.

Samples of water were taken at various intervals and analyzed for mercury. The results of these analyses are shown in Table 5.

The concentrations of mercury in all the water samples analyzed were in the 0.5 to 15 ppb range. These concentrations are approaching the limits of sensitivity of the analytical method, which accounts for some of the scatter in the data. The mercury content of water overlaying sediments having high mercury content (1,000 ppm) does not normally exceed a few parts per billion. The general trends indicate that iron is effective and the iron-sand is more effective in reducing the mercury content of water covering mercury-laden sediments.

Mercury Recovery from Sediment

A variety of methods for recovering mercury from in-place sediment or from dredged sediments was evaluated. These methods included size grading, gravity separation, flotation, roasting and leaching. A description of the methods used and the results obtained are described below.

Particle Size Separation. Sediment Samples Nos. 1 and 4 were divided into seven particle-size fractions using brass sieves. These fractions were analyzed for organic material by ashing samples of dried sediment. The results of these ashing studies and the calculated organic content of each particle size fraction are shown in Tables 6 and 7. It was subsequently determined that carbonates present in the sediments were being degraded during ashing, and that the calculated organic content was therefore too high. The organic content based on carbon and hydrogen analysis was subsequently shown to be: Sample 1 < 1%; Sample 3 ~ 5% and Sample 4 ~ 10%.

Since brass screen might reduce and amalgamate any water-soluble mercury present in the sediments or amalgamate any free mercury, bolting cloth sieves were used to separate sediment fractions to be analyzed for mercury. Sieve sizes of 60, 200 and 325 mesh were used to separate the sediment into four fractions: + 60 mesh; -60 to + 200 mesh; -200 to + 325 mesh; and -325 mesh. The fraction of sediment that passes through the 325-mesh bolting cloth sieve agreed very closely with the fraction that passed through the 325-mesh brass sieve. The percent of total solids, total mercury in each particle-size fraction and the present mercury in each particle-size fraction are shown in Table 8.

TABLE 5. MERCURY CONTENT OF WATER OVER SEDIMENT

Sediment	Overlay	Initial Hg Conc. (ppm)	30-Day Hg Conc. (ppm)	60-Day Hg Conc. (ppm)	90-Day Hg Conc. (ppm)	180-Day Hg Conc. (ppm)
Sample 1	None	0.000	0.000	0.010	0.014	0.0015
	Iron	0.001	0.000	0.010	0.010	0.0035
	Iron and Sand	0.002	0.000	0.005	0.003	0.0017
Sample 3	None	0.000	0.184	0.010	0.009	0.0013
	Iron	0.000	0.000	0.009	0.012	0.0034
	Iron and Sand	0.002	0.002	0.005	0.0052	0.0034
Sample 4	None	0.010	0.000	0.007	0.0045	0.0004
	Iron	0.006	0.000	0.004	0.0326	0.0005
	Iron and Sand	0.002	0.003	0.009	0.0033	0.0017
Sample 5	None	0.067	-	-	0.0020	-
	Iron	0.011	-	-	0.0030	-
	Iron and Sand	0.007	-	-	0.0017	-

TABLE 6. PARTICLE SIZE AND ORGANIC DISTRIBUTION IN ST. CLAIR RIVER SEDIMENT (SAMPLE 1) 50 G OF WET SEDIMENT SCREENED

Mesh Size	Dry Weight (g)	Percent of Solids	Weight of Ash (g)	Organic[a] (%)
> 20	0.087	0.39	0.039	55.20
20 to 60	0.775	3.46	0.540	30.30
60 to 100	1.019	4.57	0.882	13.42
100 to 200	1.441	6.46	1.279	11.23
200 to 270	1.114	5.00	0.964	13.44
270 to 325	0.479	2.14	0.398	16.90
< 325	17.463	78.1	15.943	8.71

(a) Based on weight lost during ashing.

TABLE 7. PARTICLE SIZE AND ORGANIC DISTRIBUTION IN SAN FRANCISCO BAY SEDIMENT (SAMPLE 4) 30 G OF WET SEDIMENT SCREENED

Mesh Size	Dry Weight (g)	Percent of Solids	Weight of Ash (g)	Organic[a] (%)
> 20	0.205	2.19	0.138	32.6
20 to 60	0.205	2.19	0.138	32.6
60 to 100	0.601	6.43	0.470	21.8
100 to 200	1.069	11.45	0.799	25.3
200 to 270	0.480	5.14	0.379	21.0
270 to 325	0.203	2.17	0.165	18.7
< 325	4.834	51.70	4.089	15.4

(a) Based on weight lost during ashing.

TABLE 8. PARTICLE SIZE DISTRIBUTION, PERCENT ORGANIC AND MERCURY CONTENT

Sample	Sample Size (dry wt-g)	Particle Size (mesh)	Percent of Total Solids	Total Mercury (µg)	Percent of Total Mercury	Percent Organic[a]
Sample 1	22.38	> 60	3.7	37.5	4.6	< 1%
		60 to 200	11.0	95.2	11.7	
		200 to 325	7.1	43.8	5.4	
		< 325	78.2	639.0	78.3	
Sample 3	11.10	> 60	5.3	6.73	4.4	~ 5%
		60 to 200	11.7	22.71	15.0	
		200 to 325	3.2	5.55	3.7	
		< 325	79.8	116.34	76.9	
Sample 4	9.35	> 60	23.1	23.8	27.1	~ 10%
		60 to 200	17.9	24.9	28.4	
		200 to 325	7.3	7.2	8.2	
		< 325	51.7	31.9	36.3	

(a) Organic content based of carbon, hydrogen analysis.

Results of the analyses of the four particle-size fractions showed little difference in mercury content in any of the fractions of sediment Samples 1 and 3. There was a small variation in the mercury content of the various fractions of Sample 4 but not enough to justify sieving as a beneficiation method.

The results indicated that no significant beneficiation of sediment could be affected by size grading.

Gravity Separation. Samples Nos. 1 and 5 were separated into density fractions, and the fractions analyzed for total mercury.

Separation was accomplished by placing wet sediment samples in centrifuge tubes containing mixtures of carbon tetrachloride and tetrabromethane. By varying the ratios of the two liquids, densities were varied from 1.6 for pure carbon tetrachloride to 3.0 for pure tetrabromethane.

Wet sediment samples were agitated and centrifuged for several minutes at 2,000 rpm. The fraction less dense than the liquid floated and was separated for analysis. The fraction which sank was transferred to a tube containing the next higher density liquid, and the fractionation was repeated.

The percent of the sediment and the percent of the mercury found in each of the specific gravity fractions are shown in Tables 9 and 10. Sediment dried in an oven or dried by repeated extractions with acetone agglomerated. These agglomerated particles, even when ground, were difficult to fractionate. Since drying would be impractical in a treatment method, studies with dry material were not pursued.

Analysis of the different fractions showed that the mercury was almost uniformly distributed throughout all the density fractions. Since a significant fraction of the mercury could not be concentrated in a relatively small fraction of the sediment, it does not appear that levigation processes, which take advantage of density and particle-size distribution, could be used practically in beneficiating mercury-laden sediments.

Flotation: Flotation studies were carried out on sediment Samples 1 and 5. A total of seven flotation reagents were used in the experimental flotation work. Mercury removal from sediment by flotation was not successful. Separations were achieved, but the concentration of mercury in either fraction, float or sink, was not appreciably different from the original concentration of mercury in the sediment (Table 11).

Leaching studies and results of specific gravity and particle size fractionation experiments indicate that mercury is present in sediments in a variety

TABLE 9. MERCURY CONTENT OF SPECIFIC GRAVITY FRACTIONS OF SEDIMENT SAMPLE 1

Specific Gravity	Weight of Fraction (g)	% of Fraction	Hg Content (µg/g)	% Hg in Fraction
< 2.1	0.009	1.7	825	9.9
2.1-2.2	0.006	1.0	466	3.7
2.2-2.3	0.006	1.0	384	3.1
2.3-2.4	0.012	2.1	350	5.6
2.4-2.5	0.028	4.9	285	10.7
> 2.5	0.506	89.3	99	67.0

(a) Average concentration of mercury.

TABLE 10. MERCURY CONTENT OF SPECIFIC GRAVITY FRACTIONS OF SEDIMENT SAMPLE 5

Specific Gravity	Weight of Fraction (g)	% of Fraction	Hg Content (µg/g)	% Hg in Fraction
2.0-2.3	0.0019	0.3	890	1.3
2.3-2.5	0.0549	12.2	602	22.6
2.5-2.61	0.3193	72.0	336	73.8
2.61-2.75	0.0680	15.2	38	1.7
2.75-3.0	0.0003	< 0.1	467	0.1
> 3.0	0.0017	0.3	225	0.4

TABLE 11. FLOTATION OF SEDIMENT

Sample Number	Reagent	% Sediment Floated	% Hg in Float
1	None	5.2	12.8
	Zephiran	9.3	17.6
		14.5	30.4
1	None	18.2	37.5
	Roccal	1.1	3.2
		19.3	40.7
1	None	13.9	35.0
	Pine Oil	8.5	17.2
	Aerosol OT and Saratoga Chips	22.6	19.2
		45.0	71.4
	Pine Oil	15.2	18.3
	Aerosol OT and Saratoga Chips	17.1	15.4
	Aerosol OT	9.1	15.3
	Roccal	3.4	7.4
	Xanthate and Dow Froth 250	4.6	12.9
		49.4	69.3
5(a)	Xanthate and Dow Froth 250	7.75	23.6
	Roccal	1.55	5.1
	Pine Oil	7.1	12.0
	Aerosol OT and Saratoga Chips	14.9	10.5
		31.3	51.2

(a) Sediment aerated before flotation study.

of physical and chemical forms. To reduce the number of chemical degrees of freedom and consequently increase the chances for separating the mercury by flotation, the sediment was treated with H_2S and $(NH_4)_2S$ in an attempt to convert all the mercury into the sulfide. No significant increase in separation efficiency was noted. Oxidation of the sediment with air prior to flotation likewise was not useful in improving the separation efficiency.

The state of the art of hydrometallurgical beneficiation of mercury-containing materials has not advanced to the point that a variety of chemical forms of mercury can be separated simultaneously. The known flotation reagents, promoters, collectors, frothers, modifiers, activators, flocculents and depressants are specific for sulfides, oxides, or metals. An extensive program of research and development would be needed to find reagents for the forms of mercury present in the sediment.

Pyrometallurgy. Experiments were conducted to ascertain whether mercury could be recovered from sediment Sample No. 1 by:

(1) Steam distillation

(2) Heating in a retort

(3) By heating to approximately 400°C in a reducing atmosphere of a yellow gas flame.

The treated sediments were tested for residual mercury. The results as shown in Table 12 indicate that roast conditions similar to those employed in extracting mercury ores would be required for sanitizing sediments. This practice would entail either inexpensive but time-consuming air dryings for water removal before roasting or a relatively expensive heat drying operation in conjunction with roasting.

TABLE 12. MERCURY RECOVERY FROM SEDIMENT SAMPLE 1 BY THERMAL TREATMENT

Treatment	Mercury Recovered (%)
Steam Distillation	1
Heating in a Retort	90
Heating in a Reducing Atmosphere	99

These preliminary studies demonstrate that conventional roasting methods used for mercury ore could be used to recover mercury from sediment. Because of the finely divided nature of the sediment, there would be no need for crushing or other preroasting treatment other than drying to minimize energy costs.

Chemical Leaching. A variety of leaching solutions was evaluated for recovering mercury from sediment. The rationale for the liquids chosen for these leaching studies was presented in Section IV. Leach liquids and the variables affecting leaching such as time, temperature and pH together with the results are shown in Table 13.

Leaching with sulfuric acid at ambient temperature did not solubilize a large fraction of the mercury in any of the sediment samples even when the pH was reduced to 1.0 or less. Hydrochloric acid was a more effective leachant, because chloride ions assist solubilization by reacting with mercury to form the soluble $HgCl_4^{-2}$ ion. A large fraction of the mercury, 95% or more, was recovered from sediment Sample 5 by leaching with 3.5% hydrochloric acid at 100°C. Hot hydrochloric acid was not as effective a leachant for some of the other sediments. A large fraction of the acid was consumed by carbonates present in Sample 1 sediment, and in significant but lesser amounts by the other sediments studied.

It appears that a hot hydrochloric acid leach might be practical for recovering the mercury value of sediments which contain little carbonate. Equipment for hot acid leaching is available and widely used by the foods industry.

Hypochlorite solution (pH 6.0-6.5) was found to be an effective leachant for all but sediment Sample 4. This leaching agent acts very rapidly, is effective at ambient temperature, solubilizes all forms of mercury in the sediment and should be relatively inexpensive when used in the vicinity of chloroalkali plants. Only sediment Sample 4, which has a large organic content, was not efficiently leached by a 1% hypochlorite solution.

Mercury leached from sediments by this process can be recovered from the leach media by metal reduction (iron), absorption on carbon, precipitation with aluminum, sulfide precipitation, or by other recently developed recovery methods. Hypochlorite is widely used in water treatment and is relatively innocuous to the aquatic environment.

TABLE 13. LEACHING STUDIES ON SEDIMENT SAMPLES

Leach Liquid	Leach Time (min)	Leach Temperature (°C)	pH	% Hg Solubilized
	Sample No. 1			
5% H_2SO_4	60	25	-	21.4
5% H_2SO_4 + 0.1% NaCl	60	25	-	27.0
5% H_2SO_4 + 1.0% NaCl	60	25	-	26.2
7.5% NaCl	4 hours	25	-	4.4
	20 hours	25	-	11.5
5% H_2SO_4	120	25	-	< 1.0
	30	100	-	< 1.0
	60	100	-	< 1.0
	120	100	-	11.7
3.5% HCl	10	25	-	0.0
	10	100	-	49.2
	20	100	-	56.9
	30	100	-	76.3
3.5% HNO_3	15	25	-	0.0
	15	100	-	15.5
	30	100	-	32.4
3.5% HNO_3[(a)]	30	100	-	70.3
3.5% HCl	30	100	-	28.6
5% NaOCl	30	25	12	64.0
	60	25	12	-
	120	25	12	70.8
5% NaOCL	30	25	6	97.3
	60	25	6	97.8
	120	25	6	98.6

TABLE 13. (Continued)

Leach Liquid	Leach Time (min)	Leach Temperature (°C)	pH	% Hg Solubilized
		Sample No. 2		
1% NaOCl	10	25	6.2	81.7
4% NaOCl	10	25	6.3	94.9
		Sample No. 3		
5% H_2SO_4	60	25	0.05	0.0
5% H_2SO_4 + 0.1% NaCl	60	25	0.10	0.0
5% H_2SO_4 + 1.0% NaCl	60	25	-	0.0
7.5% NaCl	4 hours	25	0.01	6.0
	20 hours	25	0.01	13.0
1% NaOCl	10	25	6.0	85.8
4% NaOCl	10	25	6.4	92.2
		Sample No. 4		
5% H_2SO_4	60	25	0.2	0.0
5% H_2SO_4 + 0.1% NaCl	60	25	0.01	0.0
5% H_2SO_4 + 1.0% NaCl	60	25	0.01	0.0
1% NaOCl	10	25	6.3	0.5
4% NaOCl	10	25	5.5	88.2
		Sample No. 5		
1% NaCl	30	100	-	< 2.0
2% NaCl	30	100	-	< 2.0
4% NaCl	30	100	-	< 2.0
5% H_2SO_4	30	100	-	4.7
5% H_2SO_4 - 1% NaCl	30	100	-	23.3
5% H_2SO_4	120	25	-	< 1.0
	30	100	-	4.7
	60	100	-	7.2
	120	100	-	12.8

TABLE 13. (Concluded)

Leach Liquid	Leach Time (min)	Leach Temperature (°C)	pH	% Hg Solubilized
3.5% HCl	30	100	-	97.0
3.5% HNO_3	30	100	-	98.0
3.5% HCl[(a)]	30	100	-	94.0
3.5% HNO_3[(a)]	30	100	-	3.0
3.5% HNO_3[(b)]	30	100	-	98.0
3.5% HCl[(b)]	30	100	-	2.0
5% NaOCl	30	25	12	47.9
	60	25	12	50.6
	120	25	12	51.2
5% NaOCl	30	25	6	97.3
	60	25	6	98.5
	120	25	6	97.7
3% NaOCl	2	25	6	97.0
	5	25	6	97.0
	10	25	6	95.0
	20	25	6	95.0
1% NaOCl	2	25	6	95.0
	5	25	6	97.0
	10	25	6	-
	20	25	6	97.0

(a) Consecutive leaches of the same sediment sample using first HCl then HNO_3.

(b) Consecutive leaches of the same sediment sample using first HNO_3 the HCl.

In summary the hypochlorite solutions (pH 6.0 to 6.5) appear to be effective leaching agents for removing mercury from sediments. Mercury solubilization is rapid and efficient with this leachant. Thus, if portable water-tight cofferdams were available so that the water level over a sediment could be reduced to a practical level (1 to 2 ft) then it would be practical to treat sediment in place.

SECTION VI

DISCUSSION

A discussion of the experimental results and their significance relative to the problem posed by mercury in sediment is presented in this section of the report.

Iron Overlay

Iron, an abundant element in nature, is not considered to be a health hazard. It is in fact noteworthy that iron anemia is more common in the United States than in many other countries because of the extra care taken in this country to cleanse food intended for human consumption. As a consequence, no adverse environmental effects would be expected if iron was used as an overlay to prevent mercury diffusion from sediment into the water.

These studies demonstrate that iron effectively and efficiently reduces mercuric ions and methylmercury ions to elemental mercury. In aqueous solutions a fraction of the methylmercury disproportionates in the presence of iron to form dimethylmercury. Such a conversion would be less probable in a natural environment because of: (1) the low steady-state concentration of methylmercury ions found in nature, and (2) the low probability of two methylmercury ions coming together simultaneously on the iron surface to accomplish methyl transfer. If dimethylmercury were formed it would react rapidly and quantitatively with mercuric ions to form methylmercury.

Hydrated iron oxide, formed when mercury is reduced, is an effective precipitator of mercuric ions and would aid in retaining mercury at the sediment-overlay interface. Consequently, the results of these studies together with consideration of the chemistry of iron and mercury compounds indicate that iron would be very effective in isolating mercury-laden sediment from water.

Sand or other inexpensive overlay materials act as physical barriers and are partially effective as sediment insulators. The effectiveness of the iron would be increased if the iron were covered with such a material. Sand would reduce the rate of diffusion of mercury thus allowing more time and opportunity for the mercury to contact the iron and be reduced. Sand would also prevent metallic mercury condensed on iron and the mercury ferrate from being redispersed by agitation.

Iron overlay has some disadvantages. Crushed automobile bodies would hinder subsequent dredging of a site treated by this method. Swift watercourses where mechanical disturbance of the sediment occurs could not be effectively treated by this method.

In summary the chemistry and the thermodynamics of the reactions of iron with soluble mercury are favorable. The results of these studies show that the rate of the reaction is sufficient so that an iron overlay covered with sand should be an effective barrier against mercuric ion diffusing out of the sediment into the water overlayer. The sand covering the iron should help to maintain an anaerobic condition around the iron which is apparently beneficial. The sand should prevent agitation of the iron layer, thus minimizing the chances of redispersing elemental mercury which condenses on the iron or precipitated mercury salts of hydrated iron oxide. This treatment method would be most applicable to industrial holding ponds, lakes or watercourses which are subjected to little or no bottom agitation.

Mercury Recovery from Sediment

Removal of mercury-laden sediment or the recovery of the mercury from the sediment may be determined to be a necessary action in some incidents of heavy mercury contamination. A drastic action such as dredging would seem to be premature at this time for a number of reasons. The most modern dredging equipment recovers only about 70% of the sediment. Unrecovered sediment would be dispersed over a much larger area and would likely result in an increase in the mercury content of the flora and fauna of the watercourse for perhaps several years. Dredged sediment could not be piled along the shore of the watercourse, but would have to be transported to a suitable disposal site. A lined excavation might have to be constructed for disposal. Future recontamination of surface or groundwater even then could occur from such a site. A second problem is disposal of the large amount of water associated with the dredged sediment. In most cases the water will not meet water quality standards and will require treatment before it can be returned to the watercourse.

Regardless of the problems, dredging may be judged to be an appropriate course of action. A variety of methods were screened for recovering the mercury value from sediments so that it could be used as a sterile landfill or returned to the watercourse.

Particle size fractionation and gravity separation were not effective in separating mercury from the bulk of the sediment. It does not appear that either of these commercially practiced methods for beneficiating ores could be used to recover the mercury value of sediment. Some concentrating of the mercury was achieved by flotation. However, because of the many chemical

forms of mercury in sediment and because the chemical forms vary from sediment to sediment, a new flotation scheme would probably be needed for each situation. Development of a scheme would be expensive and difficult to justify.

Sediment could be roasted using conventional equipment and methods to recover the mercury value. The energy costs would be excessive if the sediments were not dewatered before roasting. Costs of transportation of the sediment to a refinery or of constructing a facility at the site would be prohibitive. Portable mercury recovery equipment used as an accessory to a locally available cement kiln would reduce the capital equipment costs. A facility of this nature would make roasting a more attractive treatment method.

Chemical leaching is the most attractive method evaluated for recovering mercury. Hot hydrochloric acid was effective in recovering 95% or more of the mercury from sediment. However, a large fraction of the acid would be consumed by carbonate which is often present in the sediment. Hypochlorite solution (pH 6.0-6.5) was found to be even more efficient than hydrochloric acid. This leaching agent is rapid and effective at ambient temperature and does not react with carbonate. Mercury solubilized by this method could be recovered from the leachate using methods used to treat chloroalkali plant effluent. Spent leachate could be returned to the watercourse. Hypochlorite solution is inexpensive and readily available in the vicinity of chloroalkali plants where many mercury-laden sediment deposits occur.

Dredged sediment could be pumped into a pond or other treatment compound, leached, and the solubilized mercury recovered by passing the leachate through the chloroalkali plant mercury-recovery facility. The sediment could then be used for landfill. A wastewater clarifier equipped with some form of agitation would be appropriate as a leach tank.

In situations where that part of the watercourse containing the mercury-laden sediment could be isolated from the remainder of the watercourse, sediment could be leached in place. The water containing the mercury could be treated to recover the mercury. By isolating the sediment there would be no fear of contaminating a larger area of the water body. In-place treatment might be particularly attractive for recovering mercury from industrial holding ponds.

SECTION VII

ACKNOWLEDGEMENTS

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We thank Dr. Curtis C. Harlin, Jr., Robert S. Kerr Water Research Center, EPA, who served as Project Officer and provided considerable insight and guidance through this program.

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SECTION VIII

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APPENDIX

DEMONSTRATION OF HYPOCHLORITE LEACH OF IN-PLACE SEDIMENT

A site will be selected or constructed which allows the water level, the water inflow and water outflow to be controlled. This site would preferably be approximately 1 acre in area and situated close to a chloroalkali plant.

Following are major features and operations to be used in conducting the feasibility study.

Engineering Operations

(1) The water level of the test site will be dropped to 1 ft or to the lowest depth possible, to conserve and minimize chlorine use.

(2) Chlorine will be mixed with the water covering the test site using conventional chlorination equipment used in municipal chlorination operations. Varying concentrations of hypochlorite ion beginning at 0.05% hypochlorite will be used for leaching.

(3) The sediment will be agitated to a depth dictated by the depth of the mercury deposit. Agitation will be accomplished using a dragline and a device such as a subsoiler used in many farming operations.

Mercury Recovery from Leachate. Two parallel methods for recovering mercury from the water will be evaluated.

(1) The first stage in mercury recovery will employ metal reduction. The leach stream will be split. Half of the stream will be passed through a bed of iron, the second half through a zinc bed.

Iron is more environmentally acceptable, and the hydrated ferric oxide formed by mercury reduction or air oxidation is an excellent coprecipitator of mercury.

Zinc is a more efficient and rapid reducing agent for mercury and forms mercury amalgams. Its environmental acceptability is being questioned.

(2) The leachant will pass from the metal reduction through an iron pyrite bed to precipitate residual mercury as the sulfide.

(3) The leachant will then be passed through a sand filter to remove any residual particulate material.

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(4) The final step in mercury recovery will involve passing the leachant through an activated carbon bed.

(5) The clean water, which may contain residual chlorine, will be diluted to an appropriate level and returned to a stream.

Water containing residual chlorine would, in actual practice, be returned for processing more sediment.

Sampling and Analysis. The following samplings and analyses would be conducted in support of the field test.

(1) The sediment to be leached will be core sampled and analyzed for mercury to obtain an accurate measure of the mercury content of the sediment to be treated.

(2) The mercury content of the water covering the sediment will be determined.

(3) Leaching will be initiated with 0.05% hypochlorite. The mercury content of the water will be monitored continually, with leaching to continue until the mercury content of the water reaches a constant level. A mercury mass balance will determine how much mercury has been solubilized. Additional chlorine will be added in stepwise increments until an acceptable fraction of the mercury is in solution.

(4) Water processing will commence when an acceptable fraction of the mercury has been solubilized. The water will be analyzed for mercury continuously as it passes through each treatment. Water will be recycled for further treatment if the mercury content exceeds maximum allowable levels.

(5) At the completion of the treatment the sediment will again be core sampled and analyzed for mercury to determine the effectiveness of the treatment.

(6) A biologist will monitor the water body treated and the stream into which the treated water is discharged to assess the environmental impact of the treatment.

The recommended field test is divided into three phases. The tasks to be performed during each phase are described. A schedule showing the duration and manpower requirement for each task is shown in Figure 1.

SCHEDULE

FIELD TEST OF HYPOCHLORITE LEACH OF SEDIMENT

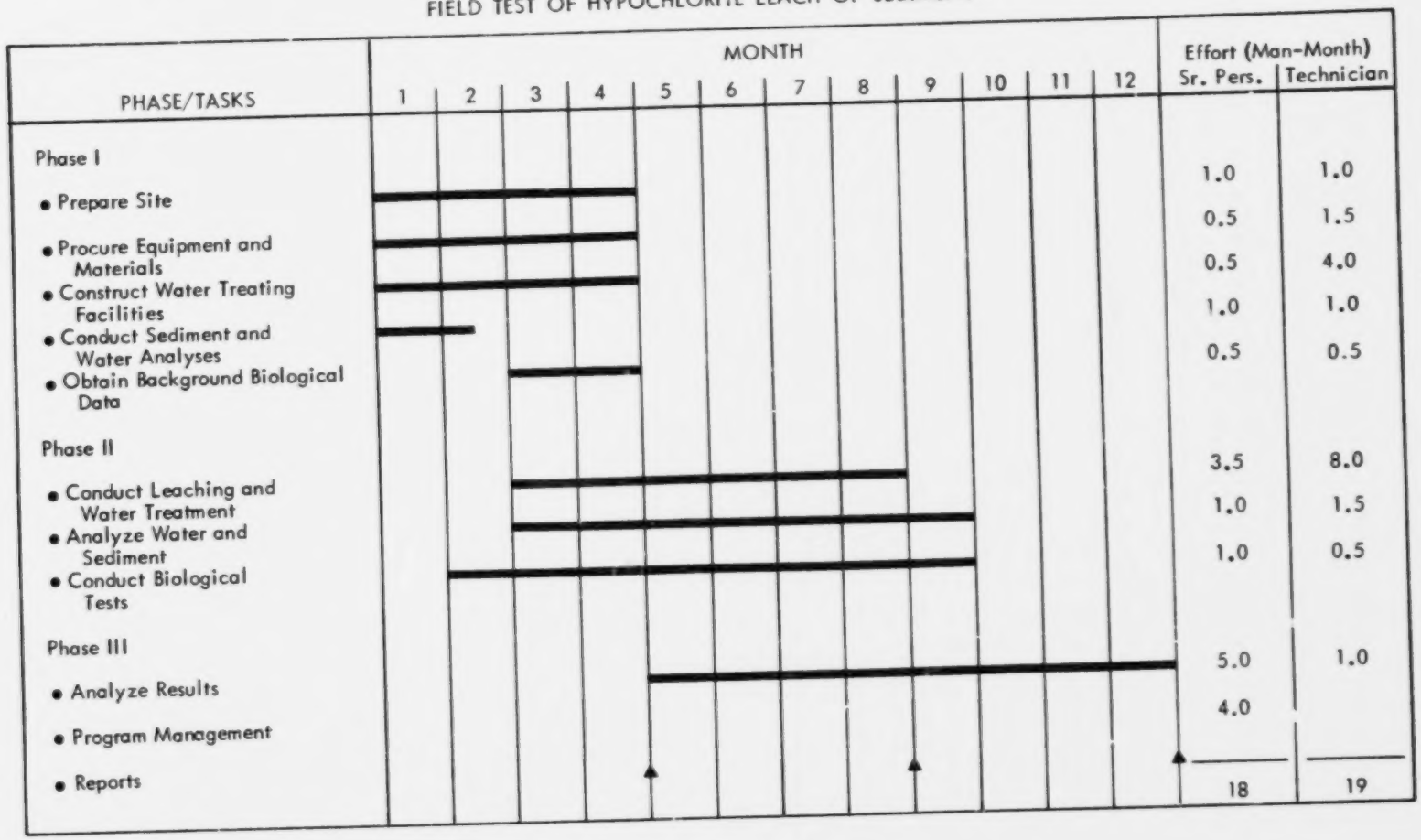

Figure 1

Phase I - Preparation of Site and Facilities. Preliminary estimates of the time required to complete Phase I are 4 months. Following are the tasks to be performed during this phase of the program.

Task 1 - Prepare Site. A temporary earthen cofferdam will be constructed around the area to be treated, by a local contractor. A pipeline will be laid over ground from the treatment pond to the Tombigbee River.

Task 2 - Procurement of Equipment and Materials. Chlorination equipment, pumps, sediment agitation equipment, and water treatment materials will be acquired, assembled and tested.

Task 3 - Construct Water Treatment Facility. Two parallel treatment processing facilities and associated pumps and piping will be designed and constructed. Each treatment process will consist of the following steps: metal reduction, sulfide precipitation, filtration and carbon adsorption. Each step of this treatment will be conducted in a 4 ft x 4 ft x 4 ft box constructed of marine plywood.

Task 4 - Water and Sediment Analysis. Water overlying the sediment will be analyzed for mercury. The sediment will be core sampled to obtain a total mercury inventory of the pond to be treated.

Task 5 - Background Biological Data. Background data on the biota of the pond to be leached and on the river which will receive the effluent of the treatment will be obtained.

Phase II - Leaching Studies. Preliminary estimates of the time required to complete Phase II are 4 months. The following tasks will be performed during Phase II.

Task 1 - Conduct Leaching Operation and Water Treatment. Leaching will be conducted by successive additions of 0.05% hypochlorite (pH 6.5) until > 95% of the mercury in the sediment has been solubilized. When leaching is completed, water treatment to recover the mercury will commence.

Task 2 - Water and Sediment Analysis. The initial water and the water after passing through each step of the treatment will be analyzed for total mercury content. Effluent which does not meet water quality standards will be returned to the pond.

At the completion of the test the sediment will again be analyzed for total mercury.

Task 3 - Biological Tests. Biological tests will be conducted on the water body treated and on the Tombigbee River below the effluent outfall to determine whether the biota was adversely affected. These studies will extend into Phase III.

Phase III - Analysis of Results. This phase of the program, together with the preparation of a final report, will require 4 months. The results of the tests and recommendations for more extensive testing or field use will be recommended.

Proposed Field Test of Iron Overlay

A site selected for field testing the iron-sand overlay for isolating mercury-laden sediment must, for the purposes of a demonstration, have the following physical and chemical features.

(1) The water should have a depth of 6 ft or greater.

(2) The area of the water body would preferably be less than 10 acres.

(3) There should not be a continuous inflow of new mercury, even at levels of 0.01 ppb.

(4) The water body must not be situated downwind from a fossel fuel combustion plant.

(5) The water must contain plant and animal life.

(6) The water body should be available for extended studies, lasting approximately 3 years.

(7) There should be no plans to dredge the water body during the study period.

Although these conditions are necessary to demonstrate the effectiveness of iron overlay in preventing pollution of the plants and fish by mercury in sediment, it is doubtful that all these conditions can be satisfied in a natural site.

It is therefore recommended that three 1/2-acre ponds be constructed. The bottoms of both ponds would be covered to a depth of 4 in. with mercury-contaminated sediment dredged from a river or lake bottom and shipped to the ponds or by spiking a real or synthetic sediment with mercury.

Water used to fill these ponds would come from the overflow of a spring-fed lake.

Following are the major features of this demonstration study.

(1) Three 1/2-acre earthen dam ponds would be constructed for use in extended studies of mercury pollution (the ponds could find future use in studying pollution by other heavy metals, pesticides, etc). One pond would be used as a control (no treatment), the second to determine the effectiveness of an iron-sand overlay, and the third pond would contain a sand overlay. The ponds could be filled by channeling part of the overflow of a lake into the ponds. The water would be treated, if necessary, to reduce its mercury content. A bypass would carry any heavy overflow around the ponds. A dike would surround the ponds to prevent natural runoff from entering the ponds. A flood gate would be installed in the dam of each pond so that the water level could be varied and the pond drained for removal of the mercury contaminated sediment at the end of the study.

(2) The bottom of each pond would be covered with 4 to 6 in. of mercury-laden sediment dredged from a contaminated lake or river bottom or synthetically prepared. These sediments should contain 10 ppm mercury or more. The sediment in one pond would be covered with 4 to 6 in. of shredded automobile bodies, in turn covered with 4 in. of sand. The sediment in the second pond would be covered with 4 to 6 in. of sand. The third pond would act as a control. All three ponds would then be filled to the desired depth and stocked with a variety of fish and plants.

(3) The mercury content of the water, fish and plants of the ponds will be monitored at regular intervals to determine the effectiveness of the iron-sand overlay. These studies should continue for 1 to 2 years, to obtain statistically reliable results.

(4) If after 2 years, the iron-sand overlay continues to function as a mercury barrier, the bottom of the control pond will be covered with the iron-sand overlay and the rate of decrease of mercury levels in the fish and plants monitored.

Work Statement

This field demonstration is divided into three phases. The tasks to be conducted during each phase are described. A schedule showing the duration of, and the manpower required, to perform each task is shown in Figure 2.

SCHEDULE

FIELD TEST IRON-SAND OVERLAY

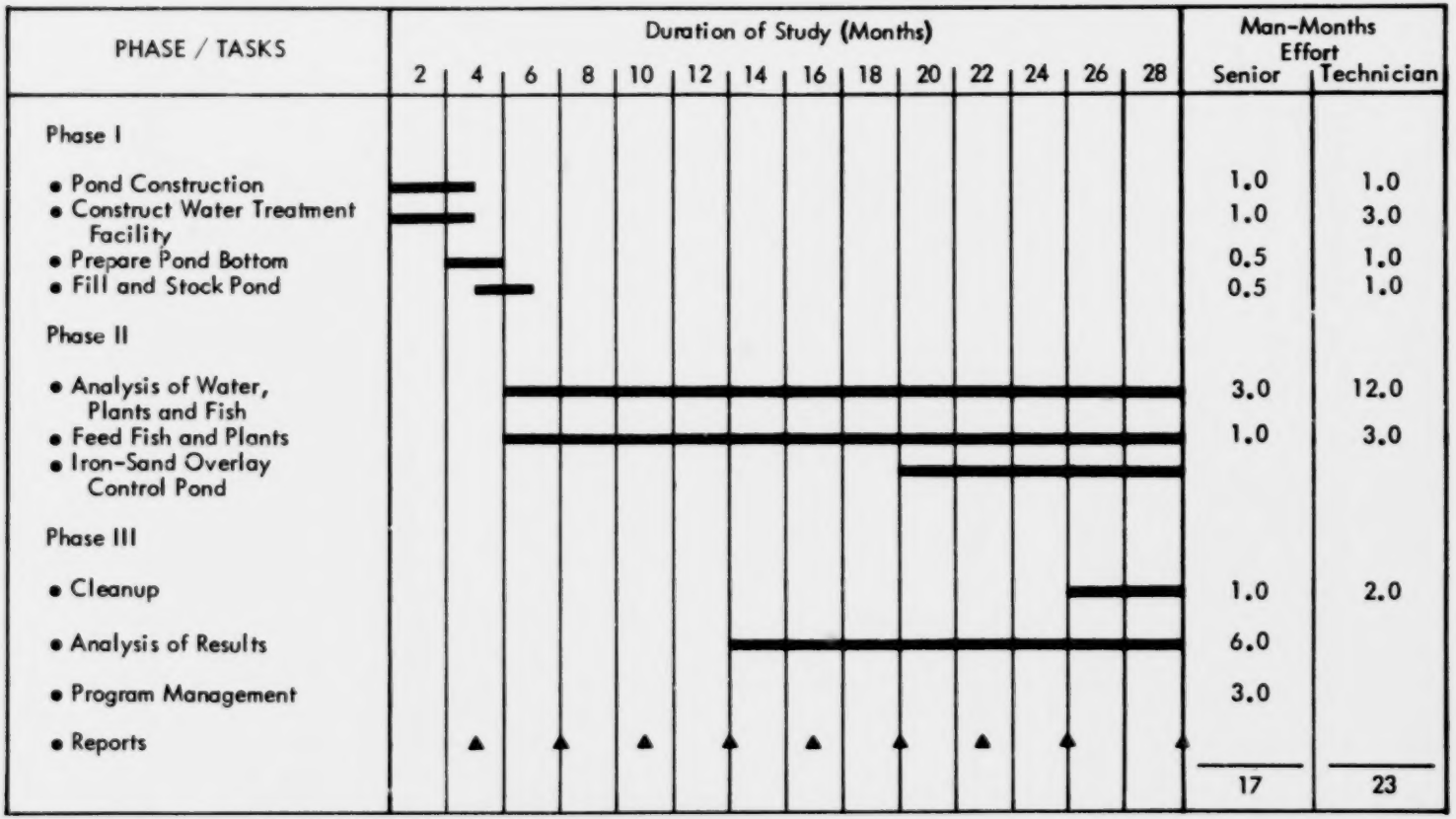

Figure 2

Phase I - Construction and Preparation of Facilities. It is estimated that 5 months will be required to complete Phase I.

Task 1 - Construction of Ponds. The major items of the construction will include the earthen dams, the water gates, the channel which feeds the ponds, a dike to prevent runoff into the ponds, and water treatment facilities. The area will be fenced to prevent accidental contamination. Given suitable weather the construction of the ponds, dike and feed canal should be completed in 2 months.

Task 2 - Water Treatment Facility. Water fed to each pond will be treated as follows:

(1) The water will filter through a 4-ft bed of shredded iron to reduce the ionic mercury to elemental mercury.

(2) It will then pass through a bed of iron pyrite to convert residual mercury to the sulfide.

(3) The water will then be passed through a sand filter to remove particulates.

This water will be analyzed continually to assure that no mercury is being added to the ponds.

Task 3 - Pond Preparation. Sediment will be dredged from a heavily sedimented lake adjacent to the pond sites. This sediment will be pumped directly to the ponds. Approximately 400 yards of sediment will be required to cover the bottoms of each pond to a depth of 6 in. This sediment will be spiked with approximately 10 ppm mercuric nitrate and mixed with a roto tiller.

One pond bottom would be covered with shredded iron and then sand, the second with only sand and the third will serve as a control.

Task 4 - Fill and Stock Ponds. The ponds would then be filled with water and stocked with a variety of fish and plants. Care will be taken to select mercury-free fish and plants.

Phase II - Monitoring of Water, Plants and Fish. This phase of the program is expected to require 1 to 1.5 years to complete.

Task 1 - Analysis of Water, Plants and Fish. Water, plant and fish samples will be taken for mercury analyses at weekly intervals during the early stages of these studies. As trends develop, these intervals will be adjusted to obtain statistically reliable data at the least expense.

Task 2 - Feeding of Fish and Plants. Mercury-free synthetic feed will be used for feeding fish to assure that external mercury contamination does not occur. A single large batch of feed will be prepared for this purpose.

Task 3 - Iron-Sand Overlay of Control Pond. If iron-sand overlay proves to be effective, the control pond will be similarly treated. The fish and plants in the newly treated pond will be monitored for mercury content at regular intervals to determine the rate of mercury loss.

Phase III - Cleanup and Analysis of Data. It is estimated that 3 months will be required for this phase.

Task 1 - Drainage and Disposal of Sediment. At the conclusion of these studies, the ponds will be drained and the sediments removed. .These sediments will be disposed of by methods judged suitable at that time.

Task 2 - Analysis of Results. Three months will be required for analysis of results and preparation of a final report. The report will contain results and recommendations for further testing or for field use.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No.

W

4. Title

CONTROL OF MERCURY POLLUTION IN SEDIMENTS

5. Report Date

6.

8. Performing Organization Report No.

Author(s)

Ivan C. Smith

Organization

MIDWEST RESEARCH INSTITUTE

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Environmental Protection Agency report number EPA-R2-72-043, September 1972.

16. Abstract

Methods are needed for controlling pollution from mercury-laden sediment deposits in the bottoms of streams and lakes. This report contains the results of exploratory studies conducted to develop control methods. Sediment samples containing 6-500 ppm mercury were collected from the St. Clair River, the Detroit River, the San Francisco Bay and an industrial holding pond. The geochemical nature of these sediments varied considerably amongst the samples. Density and particle-size fractionation, flotation, roasting and leaching were evaluated for recovering the mercury value from the sediments. Only leaching and roasting appear to have merit. Studies were also conducted to determine the rate and efficiency of the removing mercury from water by reducing mercuric and methylmercury ions with iron. Field tests for controlling mercury pollution by (1) overlaying sediments with iron and sand, and (2) by recovering the mercury by leaching with a hypochlorite solution were recommended.

17a Descriptors

Mercury,* Sediments,* Gravity Fractionation, Particle Size Fractionation Flotation, Leaching, Iron Reduction, Methylmercury, Dimethylmercury, Analytical Methods*

17b Identifiers

Sediment Treatment, Mercury Recovery, Mercury Pollution

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